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Perchloro-(dimethylene-1, 2-cyclobutanedione) and Its Solvolytic Degradation*

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Perchloro-(3, 4-dimethylenecyclobutene) has been converted to 1, 3′, 3′, 4′, 4′-pentachloro-2-methoxy-3, 4-dimethylenecyclobutene; in some solutions exposed to the air, this then gradually decomposed to perchloro-(dimethylene-1, 2-cyclobutanedione). The further spontaneous degradation of the last compound in an aqueous ethanol solution has also been investigated in order to elucidate the structures of an unstable intermediate (an adduct of ethanol to the carbonyl) and the end product (the hemi-ketal lactone ester). The physical and chemical properties of these compounds have been given and discussed. A possible bicyclic intermediate caused by the interaction between the hydroxyl group and the diagonally-positioned dichloromethylene group in above unstable ethanol adduct has been suggested in the process from the latter compound to the end product.

In a preceding paper,(1) which reported on some chemical properties of perchloro-(3, 4-dimethylenecyclobutene) (I), it was demonstrated that the double bond at the C_{1-2} position of this chlorocarbon is readily cleaved by the attack of various oxidizing agents. Although the extremely high reactivity of the corresponding hydrocarbon,(2,3) which rapidly polymerizes upon being exposed to the air, placed it beyond direct comparison, the expectation of valuable information about the hitherto little mentioned complicated triene system in chlorocarbon led us to initiate this study of the chemical behavior of I. Perchlorosubstitution positively effects a retardation of the polymerization tendency of the triene, as in the case of open-chain compounds.(4) Another reason for examining the chemical properties of I as well as of the related compounds is that the reactivity would be closely connected with both the electronic and the steric characters of the chlorine substituents in the molecule. This paper will deal with the action of some bases on I, the subsequent air oxidation of the product to a four-membered α-diketone, and the ethanolysis of the latter, which involves unique type of ring cleavage, to a lactone ester.

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* Perchlorocompounds II.

1) A. Fujino, Y. Nagata and T. Sakan, This Bulletin, **38**, 295 (1965).

2) A. T. Blomquist and F. M. Maitlis, *Proc. Chem. Soc.*, **1961**, 332.

3) W. D. Huntsman and H. J. Wristers, *J. Am. Chem. Soc.*, **85**, 3308 (1963).

4) A. Roedig, G. Voss and E. Kuchinke, *Ann.*, **580**, 24 (1953).

Results and Discussion

Compound II (m. p. 124°C), in which one of the chlorine atoms in I is replaced by a methoxy-group, was obtained almost quantitatively when I was treated for a short period with a methanolic sodium or potassium hydroxide solution containing a total of 2.5 equivalents base to I. Similar results were observed with the use of a sodium methoxide solution. Both the infrared spectrum ($\nu_{C=C}$ 1705 s and 1605 vs cm^{-1}, and 935 cm^{-1} assigned to the $\underset{|}{-C}=CCl_2$ group⁵⁾ and the ultraviolet absorption (in Fig. 1, along with that of I) of II indicate that no remarkable change either in its skelton or in the double system has occurred in the transformation of I.

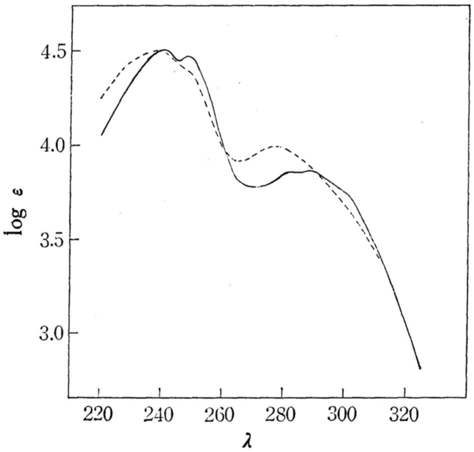

Fig. 1.
---- Perchloro-(3, 4-dimethylenecyclobutene) (I)
—— 1, 3′, 3′, 4′, 4′-Pentachloro-2-methoxy-3, 4-dimethylenecyclobutene (II)

The 1605 cm^{-1} band is the most intense one over the whole absorption range; it is approximately twice as strong as the 1705 cm^{-1} band. This suggests that two bands with the same wave number coincide in the former. In addition, the data are also in accord with the reported observation that the replacement of a chlorine substituent by a methoxy-group in some polychloro-cyclopentadiene⁶⁾ and cyclobutene⁷⁾ derivatives has caused a shift of their $\nu_{C=C}$ frequencies to a higher region. The oxidation of II with hydrogen peroxide in ether gave perchloro-(dimethylenesuccinic acid).¹⁾ (III) (m. p. 215°C (decomp.)), revealing that the location of the methoxy-group is on the ring carbon. The structural proof for III has been established by the catalytic reduction of III to a chlorine-free dicarboxylic acid (m. p. 211°C), an acid which is identical with the *meso*-dimethylsuccinic acid synthesized from 2-bromopropionic acid. Therefore, the structure shown in Chart I may, without doubt, be given to II.

II was gradually decomposed in benzene or in carbon tetrachloride, while hydrogen chloride was evolved, when the solution was exposed to the air for a long period. The product was a red oil from which scarlet crystals of $C_6Cl_4O_2$ (IV) (m. p. 167°C) were obtained. The structural evidence for its giving the four-membered α-diketone may be enumerated as follows: 1) infrared absorption: $\nu_{C=O}$ 1805 m, 1755 s; $\nu_{C=C}$ 1595 s, 1515 m cm^{-1}; 935cm^{-1} ($\underset{|}{-C}=CCl_2$).⁵⁾ 2) IV was oxidized with 30% hydrogen peroxide to the anhydride (V)¹⁾ (m. p. 119—120°C) of III. A similar type of oxidation has been reported by several authors⁸⁻¹¹⁾ for members of the substituted cyclobutadienoquinone series, sometimes as a diagnostic method for α-diketone. 3) IV was normally condensed with *o*-phenylenediamine in acetic acid to give a quinoxaline derivative (IV) (m. p. 197.5—198°C), the ultraviolet spectrum of which is shown, along with that of IV, in Fig. 2. No ring opening as in the reaction of mono-¹¹⁾ or diphenylcyclobutadienoquinone¹²⁾ with the diamine has been observed in this case.

IV may be sublimed under a vacuum and recrystallized from ether. Most interestingly, however, IV was spontaneously decomposed in a solution

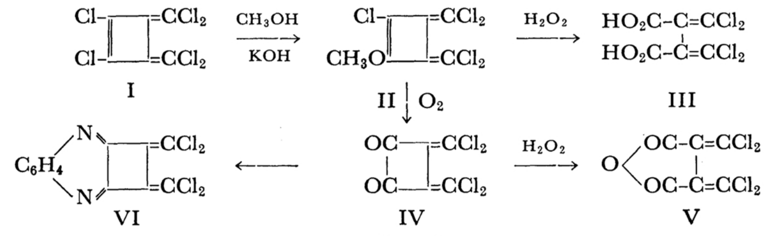

Chart 1

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5) See Ref. 1, footnote 11.

6) E. T. McBee, D. L. Crain, R. D. Crain, L. R. Belohlav and H. P. Braendlin, *J. Am. Chem. Soc.*, **84**, 3557 (1962).

7) J. D. Park, J. R. Dick and J. H. Adams, *J. Org. Chem.*, **30**, 400 (1965).

8) A. T. Blomquist and R. A. Vierling, *Tetrahedron Letters*, **1961**, 655.

9) A. T. Blomquist and E. A. LaLancette, *J. Am. Chem. Soc.*, **83**, 1387 (1961).

10) A. Roedig and R. Kohlhaupt, *Tetrahedron Letters*, **1964**, 1107.

11) E. J. Smunty, M. C. Caserio and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 1793 (1960).

12) A. T. Blomquist and E. A. LaLancette, ibid., **84**, 220 (1962).

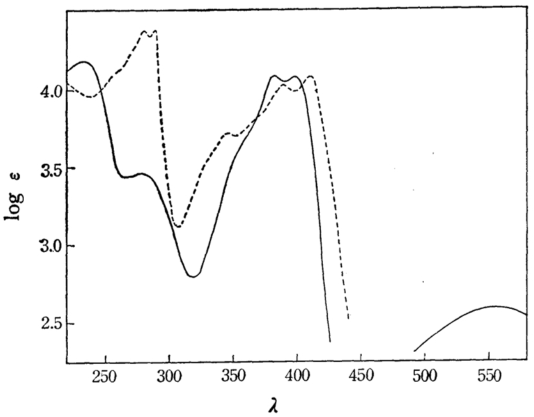
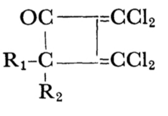
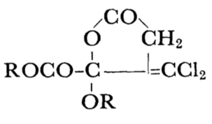


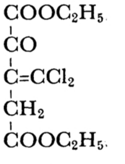
Fig. 2.
—— Perchloro-(dimethylene-1, 2-cyclobutanedione) (IV)
---- Quinoxaline derivative (VI) from IV

in the presence of ethanol and water. It has been observed that, when a small amount of 99% ethanol was added to the system, the peak heights at 234, 280, 383 and 400 (mμ) in the ultraviolet absorption of IV in cyclohexane began to lower at a markedly rapid rate, and then went on to produce, less rapidly, a new absorption peak at 335 mμ. This new peak also started to decay, after reaching a certain height, and finally became a complete transparency. In ethanol alone the original spectral features of IV disappeared too quickly for it to be precisely followed. A more detailed plot of the slower decay at 335 mμ against the time with a highly-diluted, freshly-prepared ethanol solution revealed its half life period to be ca. 30 min. This observation suggests that some unstable reaction intermediate is formed from IV and ethanol, and that the intermediate collapses a little more slowly than IV itself. The isolation of this intermediate has not been successful; the attempted procedures have resulted only in the regeneration of IV as a sublimate. It is highly probable that ethanol has first been added to one of the carbonyls, thus establishing an equilibrium between the adduct (VIIa) and the components, as has been suggested by Mallory and Roberts[13] in the thermal methanolysis of phenylcyclobutadienoquinone. Blomquist and LaLancette[9] reported a smooth ethanolysis of diphenylcyclobutadienoquinone at 25°C; it then proceeds to diethyl α, α′-diphenylsuccinate, probably via bisphenylketene. In the case of IV, however, there can be no transformation like this, for the bis-ketene formation is structurally disallowed. Uhler, Shechter and Tiers[14] also observed the instability of 3, 4-bis(diphenylmethylene)-1, 2-cyclobutanedione in ethanol near room temperature, but they provided no other information on its degradation process. The speculation about the mono-hemiketal intermediate VIIa is further supported by the observation that perchloro-(2, 3-dimethylenecyclobutanone)[15] (VIIb) absorbs the ultraviolet light at 344 mμ in cyclohexane.

IV was refluxed with 99% ethanol in order to examine the decomposition product. The reaction mixture soon turned strongly acidic, and the evolution of hydrogen chloride was observed. The chromatographically-fractionated neutral product was an oily material, $C_{10}Cl_2H_{12}O_5$ (b. p. 170°C (bath temp.)/3.5 mmHg), in a 70% yield. The hemi-ketal lactone ester formula VIIIa is the only one which rigorously accounts for its infrared ($\nu_{C=O}$ 1780m and 1730 s cm^{-1}, $\nu_{C=C}$ 1580 m cm^{-1} and 920 s cm^{-1} for $-\underset{|}{C}=CCl_2$ group[5]), ultraviolet (λ_{max}^{EtOH} 260 mμ, ε 4500) and NMR (5.64, 5.86, 8.60 and 8.73 τ for the protons in the ethoxy-group and 6.41 τ for the two protons in the $-CH_2CO-$ group) spectral properties. The chain structure (IX), the most possible alternative, may be ruled out in view of the observed high value of the first $\nu_{C=O}$ frequency. The ultraviolet absorption was drastically changed by the addition of alkali;







VII a: $R_1=OH$, $R_2=OC_2H_5$
b: $R_1=R_2=Cl$

VIII a: $R=C_2H_5$
b: $R=H$

IX

it did not reproduce the original curve on acidification. Further, the 2, 4-dinitrophenylhydrazine test proved the existence of a ketonic group in VIIIa. Both the Tollens' reagent and phosphomolybdic acid in aqueous ammonia normally reacted with VIIIa, whereas the fuchsin-sulfurous acid did not bring about a parallel result. This irregularity in the aldehyde test can well be interpreted as what may reasonably be expected if it is assumed that the dichloromethylene group in VIIIa is a potential aldehyde which, in effect, functions only in the alkaline medium. The alkaline hydrolysis converted VIIIa to a carboxylic acid, $C_6Cl_2H_4O_5$ (VIIIb) (m. p. 131°C). The evidence for the structure included: 1) neutralization equivalent: 114; 2) pK_a value: 1.65 and 4.08; 3) ultraviolet (λ_{max}^{EtOH} 254.5, ε 2100), infrared (ν_{OH} 3200, $\nu_{C=O}$ 1770, 1730; $\nu_{C=C}$ 1670 cm^{-1}) and NMR (5. 79 τ in D_2O) spectra; 4) an indication of a potential aldehyde in the test similar to those for VIIIa. An additional confirmation of the structure has been achieved by the hydrogenation of the dichloromethylene group to a methyl group, followed by an alkaline

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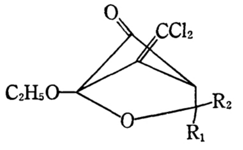
13) E. B. Mallory and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 393 (1961).

14) R. O. Uhler, H. Shechter and G. V. D. Tiers, ibid., **84**, 3397 (1962).

15) This compound will be reported in detail in the succeeding paper.

hydrolysis, presumably to β-methyl α-ketoglutaric acid (X) (the 2, 4-dinitrophenylhydrazone of its monoethyl ester: m. p. 171°C).

In the process VIIa→VIIIa, the initial hydrolysis of the dichloromethylene group β-positioned to the residual carbonyl in VIIa appears to have occurred by way of an acid chloride or its analog. It should be noted here, however, that there is is an another possibility, that the initial participation of the hydroxyl group in VIIa to the diagonally-positioned dichloromethylene moiety is more important in this degradation. Because of the enhanced puckering of the four-membered ring in VIIa due to the two severely-interacting chlorine atoms on each exocyclic methylene carbon, the hydroxyl group is made so closely accessable to the diagonal dichloromethylene or chloroethoxymethylene group as to cause the subsequent formation of a potential lactone, such as XIa or XIb. At the present stage it seems fairly difficult to conclude which one is the true transformation process. However, one piece of evidence which favors the speculation that the ring puckering makes the vinylogical chlorine substituent less reactive toward hydrolysis has been experimentally observed; the fading rate of the red color of IV in dioxan-water (9 : 1 by vol.) was much slower than in an alcoholic system. Even when the solution was heated at 100°C, the hydrolytic degradation took place very gradually. This suggests that the chlorine-substituent hydrolysis of either one or of both, in VIIa will also be slow and will not precede the formation of XI.



XI a: $R_1=R_2=Cl$
b: $R_1=Cl$, $R_2=OC_2H_5$

An inspection of the model also supports this speculation about the stereospecific approach. Perhaps, as the following step, the hydrolysis of the geminated dichloromethylene or chloro-hemiketal group and the alcoholytic cleavage of the ketone would take place almost concertedly because of its highly-strained bicyclic structure.

Other alcohols, such as methanol (1), propanol (2), isopropyl alcohol (3), *n*-butanol (4), *t*-butanol (5), *n*-hexanol (6), cyclohexanol (7) and benzyl alcohol (8), were preliminarily examined in terms of the ketone degradation. It was found that, except for 3, 5 and 8, they react with IV much like ethanol. IV was decomposed very slowly in the isopropyl alcohol solution, while no noticeable change was observed in *t*-butanol and benzyl alcohol. These definite differences in the reactivity of alcohols may be well interpreted by assuming a difference in the ease of their initial addition to the carbonyl group in IV.

Experimental[16]

1,3′,3′,4′,4′-Pentachloro-2-methoxy-3, 4-dimethylenecyclobutene (II). — A mixture of perchloro-(3, 4-dimethylenecyclobutene) (I) (10 g.) dissolved in benzene (80 ml.) and methanolic potassium hydroxide (4.8 g. of potassum hydroxide in 50 ml. of anhydrous methanol) was stirred at room temperature for 3 hr. The solution was then repeatedly washed with water, and the neutral fraction was separated. The crystalline product was collected after the evaporation of the solvent as white needles, which were recrystallized from methanol to give a material with a melting point of 118—120°C. 5.3 g. (55%). The pure sample for analysis melted at 124°C.

Found: C, 30.11; H, 1.48; Cl, 63.25. Calcd, for $C_7Cl_5H_3O$: C, 29.98; H, 1.08; Cl, 63.23%. UV: λ_{max}^{EtOH} 238(30200), 277(10000); λ_{sh} 233(28200); λ_{min} 264—267(9100), mμ(ε).

The Oxidation of II with Hydrogen Peroxide. —A reagent solution was first prepared by shaking an aqueous hydrogen peroxide solution (30%, 30 ml.) twice with ether (each 25 ml.). II (327 mg.) was dissolved in the ether containing the peroxide, after which the entire solution was allowed to stand at room temperature for 17 days. A part of the acidic fraction (37 mg.) crystallized to give a material which is, in a comparison of their infrared charts, identical with the perchloro-(dimethylenesuccinic acid) (III) previously reported.[1]

The Reduction of III to *meso*-Dimethylsuccinic Acid.—III (266 mg.) dissolved in ethanol (5 ml.) was hydrogenated with 5% palladium chloride on charcoal (200 mg.). After the absorption of the calculated amount of hydrogen, the separated acidic fraction was vacuum-sublimed (120—130°C (bath temp.)/5 mmHg) to give 34 mg. of the material with a melting point of 211°C.

Found: C, 49.44; H, 6.91. Calcd. for $C_6H_{10}O_4$: C, 49.31; H, 6.90%.

meso-Dimethylsuccinic acid was synthesized by heating a mixture of 5 g. each of 2-bromopropionic acid and of silver powder at 150—160°C in a sealed tube for 3 hr. The crystalline product was then collected from a viscous acidic oil after the solution had been kept in a refrigerator. The crystals were purified by sublimation, after being pressed between a folded filter paper, a to material with a melting point of 204—208°C. The infrared absorption of this acid was identical with that of that obtained above by the reduction of III.

Perchloro-(dimethylene-1, 2-cyclobutanedione) (IV).—The benzene (10 ml.) solution of II (2.77 g.) was shaken with oxygen gas at room temperature. A little more than one equimolar amount of oxygen was absorbed in 3 hr. While it was being kept in the open air, the solution gradually turned red and there was a slow evolution of hydrogen chloride, and the solid material crystallized out as red leaflets. The filtered crystals, after being washed with a small amount of carbon tetrachloride, weighed 1.02 g. (42%). Recrystallization from ether afforded a pure sample of diketone IV (m. p. 167°C). The yield of IV was lower when the run was carried out in carbon tetrachloride.

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[16] All meltng points given are uncorrected.

Found: C, 29.52; H, 0.44; Cl, 57.31. Calcd. for $C_6Cl_4O_2$: C, 29.31; H, 0.00; Cl, 57.68%. UV: $\lambda_{max}^{cyclohexane}$ 233—234(14700), 280(2900), 383(11500), 402—403(11500), 550—560(400); λ_{min} 270(2800), 320(600), 395(10700), mμ(ε).

The Oxidation of IV to Perchloro-(dimethylenesuccinic) Anhydride.—A mixture of a chloroform (4 ml.) solution of IV (100 mg.) and 30% aqueous hydrogen peroxide (1 ml.) was efficiently shaken and allowed to stand at room temperature for 48 hr. The neutral solid mass was then collected and recrystallized from petroleum ether to give a sample of V with a melting point of 119—120°C. 14 mg. The infrared absorption is identical with that previously reported.(1)

1, 2-Bis (dichloromethylene) cyclobuta [b] quinoxaline (VI).—A mixture of IV (105 mg.) and *o*-phenylenediamine (46 mg.) was heated in acetic acid at 100°C for one hour. After it had been cooled, the solid product was filtered under reduced pressure and recrystallized from ethanol as long yellow needles (m. p. 197.5—198°C). 79 mg.

Found: C, 45.56; H, 1.57; N, 8.75. Calcd. for $C_{12}Cl_4H_4N_2$: C, 45.32, H, 1.27; N, 8.81%. UV: λ_{max}^{EtOH} 270—271(23700), 279(23300), 335—337(5400), 378(10500), 400—402(12200), mμ(ε). IR: $\nu_{C=C}^{Nujol}$ 1665 s, 1640 m, 1610 s, 1583 m cm.$^{-1}$

The Ethyanolytic Degradation of IV to the Hemiketal Lactone Ester (VIIIa).—IV (4.79 g.) was, after the addition of ethanol (40 ml.), heated on a water bath for 10 min. The neutral fraction was then separated and chromatographed on silica gel (10 g.) with benzene. The light yellow main fraction (4.64 g.) was vacuum-distilled at 170°C (bath temp.)/3.5 mmHg to give a colorless oil of VIIIa.

Found: C, 42.35; H, 4.49. Calcd. for $C_{10}Cl_2H_{12}O_5$: C, 42.42; H, 4.27%.

The Hydrolysis of VIIIa to the Hydroxylactone Acid (VIIIb).—To VIIIa (381 mg.) an aqueous sodium hydroxide solution (N, 2.8 ml.) was added; the mixture was then shaken for 10 min. at room temperature. The acidic fraction, when separated in the usual manner, furnished a viscous oil (207 mg.) which gradually solidified to give colorless fine crystals, (m. p. 128—131°C). Repeated recrystallization from chloroform afforded a sample of VIIIb with a melting point of 131—133°C.

Found: C, 31.88; H, 2.04. Calcd. for $C_6Cl_2H_4O_5$: C, 31.74; H, 1.78%.

The Hydrogenation of VIIIb and the Subsequent Hydrolysis to *β*-Methyl-*α*-ketoglutaric Acid (X).—The ethanol (5 ml.) solution of VIIIb (1.72 g.) was shaken with hydrogen under atmospheric pressure in the presence of 5% palladium chloride on charcoal. After the calculated amount of hydrogen had been absorbed, the catalyst was filtered off and the filtrate was passed through a column packed with aluminum oxide (5 g.). After the solvent had been removed, the residual oil was vacuum-distilled at 100—120°C (bath temp.)/5 mmHg.

Found: C, 54.96; H, 7.58. Calcd. for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46%. IR: $\nu_{C=C}$ 1800, 1725 cm.$^{-1}$

The distillate above (230 mg.) was heated with an aqueous sodium hydroxide solution (0.1 N, 20 ml.) for 10 min. on a water bath; the acidic product was then continuously extracted with ether. After the ether had been removed After the solution had been dried, the hygroscopic residue remained oily and its infrared spectrum showed a very intense and broad ν_{OH} band.(17) This material (70 mg.) was heated with 2, 4-dinitrophenylhydrazine (60 mg.) in ethanol, the quantity of which was enough to dissolve both of them. A small amount of water (2 ml.) was added, and the whole solution was then strongly heated under refluxing for one hour. The acidic fraction was separated and chromatographed on silica gel, with a developing solvent of benzene - methanol - acetic acid (25 : 8 : 4 by vol.), to acid crystals with a melting point of 167—171°C.

Found: C, 45.67; H, 4.33; N, 15.23. Calcd. for $C_{14}H_{16}N_4O_8$: C, 45.65; H, 4.38; N, 15.21%.

We wish to express our thanks to Mr. Junichi Goda and Miss Hiromi Tokuda of Osaka City University for his elemental analyses and her infrared spectra measurement, and also to Dr. Kazuo Tori of Shionogi Research Laboratory for NMR spectra data.

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17) Although G. Cauquil reported the melting point of 167°C for X (*Compt. rend.*, **208**, 1156 (1939)), it is doubtful whether the precursory compound (m. p. 186°C), obtained by the oxidation of pulegon with selenium oxide, really has a triketone structure. Our infrared datum indicated the presence of alcoholic group in this compound.